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Electro-oxidation of Formic acid on FeCo/C Electrocatalysts in Membraneless Fuel Cells

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Abstract— **This paper presents the continuous flow operation of membraneless sodium perborate fuel cell using FeCo/C catalyst in alkaline/acid media. A series of carbon supported FeCo bimetallic electrocatalysts with varying Fe:Co composition ratio were prepared and were evaluated in membraneless sodium perborate fuel cell. In this membraneless fuel cell, formic acid is used as a fuel in alkaline media and perborate is used as an oxidant in acidic media. FeCo/C catalyst acts as an anode and Pt/C act as cathode. At room temperature, the laminar flow based microfluidic membraneless fuel cell can reach a maximum power density of 33.8 mW cm^{-2} with a fuel mixture flow rate of 0.3 mL min^{-1}. The results showed that the prepared nanocatalysts are considered as promising anode catalyst for electro-oxidation of formic acid in membraneless sodium perborate fuel cell.**

Keywords- **Alkaline/acid media; FeCo/C catalyst; Formic acid; Membraneless sodium perborate fuel cell**

I. INDRODUCTION

Fuel cells are electrochemical devices which convert chemical energy directly to electrical energy with high conversion efficiency and low environmental pollution. In recent years, numerous studies have been focused on membraneless fuel cells. However, despite substantial progress, a number of challenges remain. One of these is the slow electro-oxidation kinetics of fuels on anode catalysts that reduces the energy conversion efficiency. This mainly caused by the poisonous intermediates (primarily CO) that are irreversibly adsorbed on the catalyst surface and the resulting impeded accessibility of the catalytic sites by fuel molecules [1].

The oxidation of formic acid is shown to proceed via various pathways including (i) dehydrogenation (direct) pathway producing CO_2 and (ii) dehydration (indirect) pathway producing the poisoning CO intermediate. Several strategies have been suggested to promote the direct oxidation pathway at the expense of the CO formation [2]. Among problems that still need to be overcome are insufficient electro-catalytic activity of the anode catalyst for formic acid oxidation and catalyst deactivation due to formic acid oxidation on noble-metal catalysts that generates intermediates such as CO that can be adsorbed on the noble metal catalysts' surface. Although Pd/C electrocatalyst exhibited much better activity than Pt/C, its activity was still not satisfactory, and more importantly its durability was in urgent need for further improvement because of rapid deactivation of this catalyst. Hence, it is important to develop new catalysts with high activity and stability for formic acid oxidation. In this context, materials in a highly dispersed form have found applications in the areas of catalysis and electrocatalysis where advantage is taken of their high surface to volume ratio to increase overall performance, while minimizing costs of often expensive metal and its alloy constituents [3]. Anode catalyst selection is pivotal to promote high power densities via formic acid electro-oxidation. In the past decades, various anode catalysts, such as single crystals of noble metals, single crystals modified with non-noble metals, Pt-free catalysts, and Pt-based metal alloys, have been tested. The current research direction is to develop alternative catalysts including the use of non-noble metal, as well as platinum alloys. Non-noble transition metals including iron and cobalt are much more economical compared with the other metals but they produce an inadequate oxygen reduction reaction (ORR) activity.

In our previous work, a microscale membraneless sodium perborate fuel cell (MLSPBFC) was fabricated on poly(dimethylsiloxane) (PDMS) and its performance was evaluated under different operating conditions[4, 5]. Standard microfabrication techniques were used to develop the device. In this present work, formic acid is used as a fuel at FeCo/C anode and sodium perborate is used as an oxidant at Pt/C cathode under "alkaline anode and acidic cathode" conditions. Research into formic acid has received great attention and has been considered as a replacement candidate for methanol as fuel in fuel cells. This is due to its high electrochemical activity arising from its non-toxicity, non-flammability and its ability to facilitate the transport of proton within the anode catalyst [6-9]. The experiments described in this study show that membraneless sodium perborate fuel cells are media flexible; they can be operated in all-acidic, all-alkaline, alkaline anode and acidic cathode or vice versa. In this work we observed that the alkaline anode/acidic cathode configuration leads to a very high measured open circuit potentials (OCP) which is in good agreement with the OCP which is achieved in our previous work, while other combinations were result in very low OCPs as a result of the pH dependence of standard electrode potentials. The flexibility of membraneless fuel cells to function with different media allowed the successful operation of mixed alkaline and acidic fuel cells. The membraneless microfuel cell system investigated in this study seems to be a good candidate for feasible application because its performance is comparable to an air-breathing DMFC. In addition, the development of FeCo/C catalysts to accelerate the efficiency of MLSPBFC will be the focus of this study.

II. EXPERIMENTAL PROCEDURE

The materials and chemicals used during the tests are listed as follows: Iron powder (CAS No: 7439-89-6) and cobalt powder, <10µm, 98% (CAS No: 7440-48-4), Merck, India, Graphite plates (Kriti Graphite), 5% Platinum on Carbon type 5T18 paste from Johnson Matthey Catalysts, India. All other materials and chemicals used throughout the tests are listed as follows: HCOOH (98%, Merck), $NaBO_3 \cdot 4H_2O$ (99%, Riedel), NaOH (98%, Merck) and H_2SO_4 (98%, Merck). All experiments were conducted at room temperature using formic acid in deionised water as a fuel and sodium perborate in deionised water as an oxidant and 1M NaOH and 1M H_2SO_4 in deionised water as electrolytes.

A. Catalyst deposition

For all the experiments of MLSPBFC, unsupported platinum black nanoparticles are applied to the sides of the graphite plates to act as cathode that line the microfluidic channel. The catalyst suspension for cathode were prepared by mixing at a concentration of 6.0 mg ml^{-1} Pt black nanoparticles (Alpha Aesar) in a 10 wt.% Nafion solution (Nafion stock solution: Dupont, 5% (w/w) solution). This mixture was sonicated and applied to the side faces of the graphite plates at a loading of 2 mg cm^{-2}. Then solvent was evaporated by the use of a heat lamp for uniform loading. The catalyst suspensions for anode were prepared by mixing at a concentration of 8.0 mg ml^{-1}. A series of carbon supported Fe_xCo_{100-x} (x = 30, 40, 50 and 60) bimetallic electrocatalysts with varying Fe:Co composition ratio were prepared in a 10 wt.% Nafion solution. This mixture was sonicated and applied to the side faces of the graphite plates at a loading of 2 mg cm^{-2}. Then solvent was evaporated by the use of a heat lamp for uniform loading.

III. RESULTS AND DISCUSSION

In this present work we consisted within the flexibility and the performance implications of operative MLSPBFC beneath "alkaline-acidic media" using carbon supported Fe_xCo_{100-x} (x = 30, 40, 50 and 60) as an anode and Pt/C as cathode. In recent years, the effect of operative streamline flow primarily based fuel cells in alkaline/ medium is highly focused [10, 11]. The performance of MLSPBFC employing a fuel stream of 2 M Formic acid in 0.5 M NaOH and an oxidant stream of 0.1 M perborate in 0.5 M H_2SO_4 was investigated.

Alkaline-acidic media allows energy to be obtained both from formic acid electro-oxidation and from acid/alkali electrochemical neutralization reactions, as evident from the overall cell reaction Eq. :

Anode: $HCOO^- + 3OH^- \rightarrow CO_3^{2-} + 2H_2O + 2e^-$ $E^\circ = -1.17$ V (1)
Cathode: $3H_2O_2 + 6H^+ + 6e^- \rightarrow 6H_2O$ $E^\circ = 1.78$ V (2)

Overall: $HCOO^- + 3H_2O_2 + 6H^+ + 3OH^- + 4e^- \rightarrow CO_3^{2-} + 8H_2O$ $E^\circ = 2.95$ V (3)

In this alkaline-acid media configuration, the combination of two galvanic reactions yields a desirable high theoretical OCP of 2.95 V. Note that the inherent value of the electromotive force of the MLSPBFC is higher than that of the HFC (1.23 V) and the PEMFC or DMFC (1.21 V). However, because of the overpotentials resulting from the slow kinetics of peroxide reduction and formic acid oxidation, the open circuit potential is reduced to a measured value of 2.02 V (Fig. 1). In the alkaline anode/acidic cathode configuration both OH^- and H^+ are consumed at the anode and cathode, respectively, at a rate of two for each molecule of formic acid.

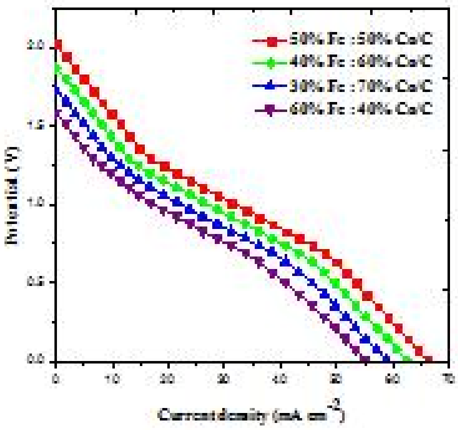

Figure 1. Polarisation curves of MLSPBFC with an alkaline anode and acidic cathode (alkaline-acidic media) at room temperature. [Fuel]: 2 M formic acid + 0.5 M NaOH. [Oxidant]: 0.1 M perborate + 0.5 M H_2SO_4

The electrocatalytic performance of the FeCo/C bimetallic catalysts was found to be increasing with the increasing percentage composition of Fe and it reaches a maximum current density and power density values at bimetallic electrocatalyst composition of $Fe_{50}Co_{50}$/C and on further increasing the percentage of Fe the current density and power density values decreases. The maximum current density was observed at the $Fe_{50}Co_{50}$/C electrode, indicating the highest electrocatalytic activity of $Fe_{50}Co_{50}$/C among the series of carbon supported Fe_xCo_{100-x} bimetallic electrocatalysts. The alkaline-acidic media results a power density maximum of 33.86 mW cm^{-2} at a cell potential of about 2.02 V as shown in Figure 2.

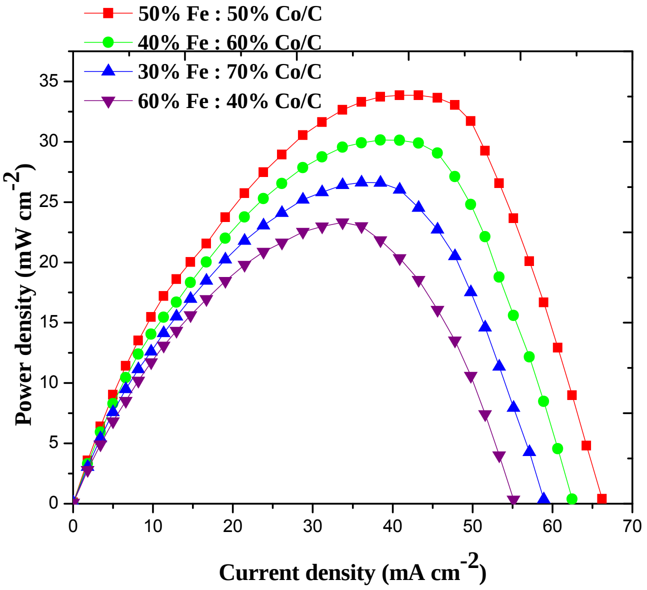

Figure 2. Power density curves for overall cell performance of MLSPBFC operating in alkaline anode acidic cathode. For all experiments the fuel stream is 2 M formic acid, and the oxidant stream is 0.1 M perborate in the respect media.

The higher power densities in alkaline-acidic media are a direct result of higher overall cell potentials due to the unprecedented ability to operate the anode and cathode at different pH in an MLSPBFC.

IV. CONCLUSIONS

In this membraneless fuel cell, formic acid is employed as a fuel at Fe_xCo_{100-x}/C anode and sodium perborate is used as an oxidant at Pt/C cathode for the first time beneath "alkaline-acidic media". The experiments represented in this study show that membraneless sodium perborate fuel cells are media flexible; they can be operated in all-acidic, all-alkaline, or even alkaline-acidic media. In this work, we tend to determine that the alkaline anode/acidic cathode media ends up in a high measured OCP of 2.02 V, while other combinations results in very low OCPs as a result of the pH dependence of standard electrode potentials. The electocatalytic activites of the Fe_xCo_{100-x}/C bimetallic electrocatalysts towards formic acid oxidation were examined. Within the series, $Fe_{50}Co_{50}/C$ were found to exhibit the best catalytic activity with maximum current density and power density value. At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 33.86 mW cm^{-2} beneath alkaline anode/ acidic cathode media and it was achieved by using $Fe_{50}Co_{50}/C$ composite catalyst as anode and Pt/C as cathode.

Further the MLSPBFC has the benefits of their miniature sizes, simplicity of fabrication, use of aqueous fuel, and good cost efficiency. We tend to expect that the MLSPBFC is also a promising candidate for sensible fuel cells to ascertain a clean and sustainable energy future.

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